APPENDIX C

Response of CARB Staff to Major Comments Received on Its Draft Report "The Ozone Weekend Effect in California"

In October 2000, the California Air Resources Board released a draft copy of a report summarizing various investigative data analyses conducted in-house to gain additional insights into the cause(s) of the Ozone Weekend Effect. This draft report, entitled "The Ozone Weekend Effect in California", consisted of two volumes - a Staff Report (SR) and an accompanying Technical Support Document (TSD). The SR was written for policy makers and general scientists. The TSD was written to communicate the more technical details of the staff analyses.

CARB staff received comments on the draft report until January 2001. External comments were received from Air Improvement Resource, Inc. (AIR) on behalf of General Motors Corporation and from Envair on behalf of the Western States Petroleum Association (WSPA). The full texts of these comments are presented in Appendix A and Appendix B, respectively. CARB staff has considered the internal and external comments on the draft Staff Report and has created the draft final Technical Support Document that this Appendix is a part of. The staff is grateful to all the people who contributed their time and expertise to comment on the draft report. Their efforts have resulted in this improved draft final report that will go out for peer review and additional external comments.

The common themes contained in the comments were: 1) the existing data demonstrate that the NO_X Reduction hypothesis best describes the Ozone Weekend Effect, 2) additional data collection efforts are not needed (and if collected, are not likely to change conclusions about the dominant cause of the Weekend Effect), and 3) photochemical modeling will answer the remaining questions. In general, it is staff's opinion that most of the existing data (experiments) were not collected (conducted) in a manner to specifically address various hypotheses of the Weekend (WE) Effect. The existing data do provide substantial support for the NO_X Reduction hypothesis but, just because the amount of currently available data needed to test the NO_X Timing or Carryover Aloft hypotheses is very limited, that does not mean those hypotheses are not valid or significant. The current air pollution databases were largely developed to support documentation of long-term trends or short term episodes for modeling. For example, meteorological variations exert the most dominant influence on ambient concentrations from day to day. Thus, short, episodic field studies do not have the robustness to filter the meteorological variations from the WE Effect. From the particulate matter (PM) perspective, the standard one-in-six day sampling schedule and variable lag times in laboratory analysis for the typical filter-based sampling create background noise from which it is difficult to extract a robust WE Effect signal for PM. Lastly, staff has reservations about the direct applicability of photochemical modeling results for specifically addressing WE Effect issues. The current state-of-art PM models have not been thoroughly validated under a variety of conditions. In general, photochemical modeling applications must appropriately address carryover aloft, temporal and spatial variations in emissions, photochemistry under low NO_X conditions, and model performance in creating initial conditions to definitively characterize the

relative influence of the various factors potentially contributing to the Ozone WE Effect. With refinements to better address the hypotheses, models will serve as a valuable tool for addressing the causes (and relative contributions) of the WE Effect.

The purpose of this Appendix is to explicitly respond to the major external comments and to provide an indication why, or why not, the staff chose to reflect them in the draft final report. To facilitate a comparison of the specific comments and the staff's position, the comments and suggestions are presented in order within each comment letter.

Major Comments from Air Improvement Resource, Inc. (see Appendix A for full text)

1) While the draft material lays out several hypotheses that have been offered to explain the ozone weekend effect, it does not go far enough in evaluating the various hypotheses with existing data. AIR believes that the case for Hypothesis #1 (NO_X reductions) as the primary cause of the weekend ozone increase is much stronger than the case for any of the other hypotheses. In addition, the proximate modeling currently planned by the Coordinating Research Council will be able to evaluate many of the key issues related to the various hypotheses in the near future. Thus, staff and the ARB will be able to evaluate the implications of the weekend ozone phenomenon for NO_X reductions in California's ozone control strategy in the reasonably near future rather than waiting for several years.

1a) The CARB staff was cautious in coming to their conclusions for a couple of reasons. First, the physical and chemical processes associated with ozone and particle pollution are very complex and our understanding of the processes and the data available to evaluate them are still incomplete. Although the available data are consistent with the NO_X reduction hypothesis, the currently available data are generally insufficient to determine how well the other hypotheses explain what we observe. Although staff suspects that the NO_X reduction is a major factor in the Ozone Weekend Effect, the relative influence of the potential factors cannot be established yet. Because the available evidence is consistent with several hypotheses, staff is reluctant to conclude, based on circumstantial evidence, that NO_X reduction is the cause of the WE Effect when other processes may have a significant role. Second, modeling is a tool used to help decision-makers; it is not a full and complete replication of what is actually occurring in the atmosphere. In fact, many of the modeling limitations tend to be in a direction that underestimates the influence of NO_X emissions. Staff does not subscribe to the theory that the atmosphere operates in a specific manner because the model says so. Models are our best current representation of atmospheric processes and are continually being updated as new information and more efficient computing techniques become available. The modeling results however must always be interpreted within the context of the limitations of the model for representing specific. A new chapter (Ch. 9) has been added to the TSD to raise modeling issues associated with accurately addressing potential factors in the Ozone WE Effect. Staff is eagerly anticipating the results of modeling applications that are well-designed to test various hypotheses of the cause(s) of the Weekend Effect. These results, even with their limitations, will help guide future refined efforts to isolate the cause(s) of the Weekend Effect.

2) Unfortunately, several key pieces of information in the TSD or in the original ARB or ARB-sponsored studies are left out of the Staff Report. Thus, the draft conveys more uncertainty than is necessary based on a fuller account of the available data.

2a) There may be an element of caution in the Executive Summary but it is also evident from the TSD that many of the observations do not paint a consistent picture of the Weekend Effect at all times and in all places. Some of the data available for evaluating the hypotheses are limited in scope and robustness, and definitive conclusions on some of the hypotheses are not appropriate at this time. Staff has reviewed and revised the material to ensure a more complete connection between the Staff report and the technical support document.

Comments on ARB strategy

3) While ozone has been reduced substantially in California, there are several problems with the SR characterization of the "success" of concurrent VOC and NO_X reductions. …Figure 1 shows that ozone decreases occurred prior to the start of NO_X controls. …The common element is, thus, VOC control. …Knowledge of the balance between recent VOC and NO_X reductions is critical to understanding whether California's NO_X controls, once initiated, have helped or hindered the ozone reductions in various air basins. …Although the chemistry that causes this phenomenon is well-accepted, it has been difficult to deal with in the public policy arena. Many years ago, Dr. Jim Pitts wrote that this phenomenon is "the curse of control officials."

3a) Ozone, whether by maximum concentrations or by number of Stage I Episodes, has declined in a steady manner before and after automotive NO_X controls began in 1975. If NO_X controls were detrimental, or have become detrimental, the rate of improvement would have slowed throughout the 1980s and 90s. Furthermore, if more typical (less extreme) trend statistics are used (e.g., number of NAAQS violations), ozone has in fact declined at a faster rate during the period of greater NO_X control (see table and figure below). The most recent emission inventory numbers indicate that ROG controls have equaled or outpaced the NO_X controls. Staff agrees that the limited amount of ambient NMOC data and uncertainties about the accuracy of O_3, NMOC, and NO_X monitoring methods (especially prior to 1980) make it difficult to assess previous trends. Furthermore, the ozone trends are not consistent among the various air basins and so additional factors may be involved. The dual nature of the ozone impacts resulting from NO_X emissions is well known but the quote of Dr. Pitts is somewhat misleading. Dr. Pitts has always advocated NO_X controls in addition to NMOC controls because NO_2 photolysis is the only known source of atomic oxygen necessary for the formation of ozone in the troposphere (Pitts et al., 1983; Finlayson-Pitts, 1993; Finlayson-Pitts, 2000).

Changes in Ozone[1] Relative to Variations in ROG and NO_X Emissions[2] in the South Coast Air Basin

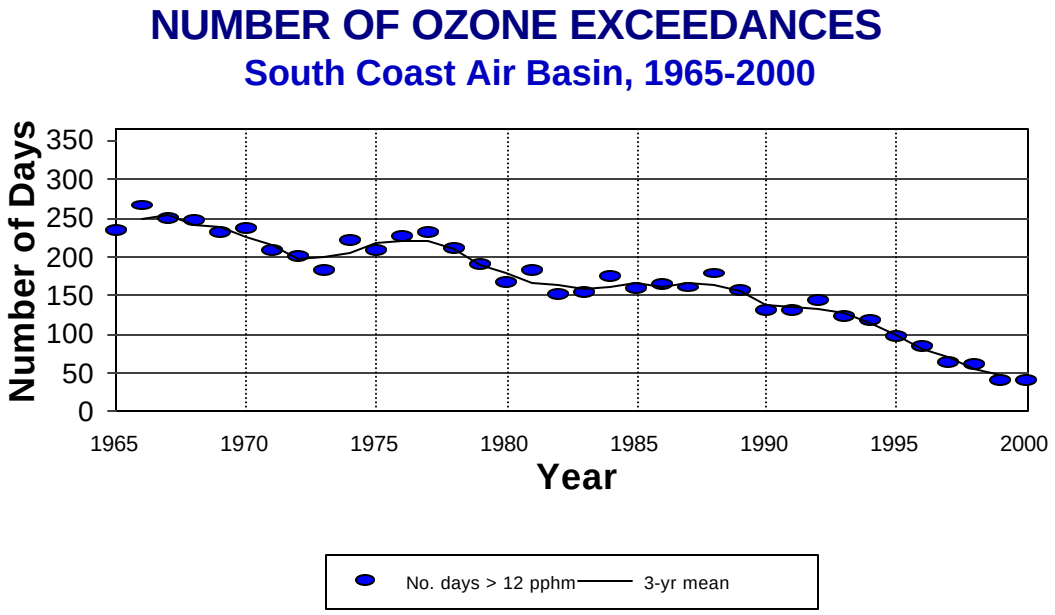
	1975	%)[3]	1980	%)	1985	%)	1990	%)	1995	%)	2000
ROG (tpd)	2882	-15	2452	-2	2407	-23	1850	-25	1374	-21	1092
NO_X (tpd)	1850	-4	1780	+8	1923	-7	1780	-17	1473	-18	1208
ROG/NO_X[4]	4.5	-11	4.0	-10	3.6	-17	3.0	-10	2.7	-4	2.6
O_3 (days)	218	-17	180	-8	166	-16	139	-28	100	-61	40

1 - number of days when the national ambient air quality standard (>12 pphm,1-hr avg.) was violated somewhere within the air basin

2 - tons per day of reactive organic gases or oxides of nitrogen based on EMFAC2000 model (source: The 2001 California Almanac of Emissions & Air Quality)

3 - percent change during 5-year period

4 – molar ratio (CH_4 /NO_2); mass ratio adjusted by molecular weights (46/16).



4) …the SR posits that there may be a difference between periodic NO_X reductions that occur each weekend and strategic NO_X reductions that would produce steady NO_X reductions on both weekdays and weekends. This appears to be a distinction without a difference. …If ARB staff has specific reasons (other than the hypotheses listed) to believe that the two day reductions in NO_X associated with weekend activity do not mimic longer-term NO_X reduction strategies, the report should document those reasons so they may be evaluated and tested.

4a) Staff concurs that carryover primarily involves ozone and hydrocarbons because NO_X tends to react out faster than ozone or hydrocarbons. That is not to say that there is no carryover of nitrogenous compounds or that they cannot re-enter the photochemical system. Recent work by Mochida (2000) and Saliba (2000) indicates the potential for nitric acid to revert back to NO_2 and active involvement in ozone photochemistry. Furthermore, some ozone data collected by lidar at El Monte Airport during SCOS97 indicate that ozone formation can begin above the surface mixing layer as soon as sunlight is present and before atmospheric mixing

processes can carry fresh emissions up to that ozone layer. Obviously for this to occur, there needs to be a source (carryover) aloft of NO_2.

Staff believes there is a distinct difference in the impacts from a decline in NO_X emissions on a weekend and from a consistent reduction at all times of the day by a NO_X control strategy. The weekend transition includes changes in the temporal and spatial patterns that do not occur under a control program.

The comment focuses on the limited carryover of NO_X over a 2-day period (i.e., weekend) because of its reactivity. The staff does not strongly disagree (conventional wisdom says NO_X carryover is very limited although, as described in a preceding paragraph, new measurements are implying this is an area to keep an open mind). The focus of staff's position is not on the NO_X carried over (or not carried over) after two days of declining emissions but on the interaction between the carryover of ozone (and NMOC) and the fresh NO_X emissions. The amount of fresh NO_X emissions (primarily in the form of NO) plays a crucial role in whether the day's photochemical processes begin with an initial baseline of ozone or not. The earlier start in the photochemistry on weekends when NO emissions are reduced allows more time for ozone formation before the process becomes precursor- or light-limited.

Magnitude of the weekend effect

5) It is clear that higher weekend ozone will be an even greater concern for achieving any 8-hour ozone standard than it is for a 1-hour standard.

5a) The remanded 8-hour ozone standard is exceeded on more days than the national 1-hour standard. Many people have anticipated that the 8-hour O_3 concentrations would be more difficult to reduce than peak 1-hour concentrations if NO_X controls are involved because the fresh NO emissions would tend to help reduce one or more shoulders of the 8-hour O_3 peak. However, in-house analysis (Larsen) indicated that, although more areas would violate the proposed 8-hour standard, it is only slightly more stringent than the current national 1-hour standard (114 ppb vs. 124 ppb). The 8-hour and 1-hour O_3 concentrations are highly correlated and it is anticipated that peak concentrations of both averaging periods would decline together. This would be especially true in cases involving transport downwind of urban areas. As reductions of ozone precursors and ozone occur in the urban areas, the ozone concentrations in downwind areas associated with transport would decline commensurately.

Comments on causes of the weekend effect

6) …periodic NO_X reductions on weekends should mimic the steady NO_X reductions from strategic regulations.

6a) This third point of this section in the comment letter actually quotes the position of some people but does not represent the position of staff. For the staff position on this point, see response 4a).

Comments on NO_X reduction hypothesis

7) The short version [of the NO_X reduction hypothesis] in the Executive Summary that is noted above leaves the impression that the basis is only "smog chamber" experiments and specifically states that "if this complex air basin acts like a simple smog chamber, then reducing NO_X emissions should (hypothetically) promote ozone formation." In fact, the basics of ozone formation that are represented in the ozone isopleths of an EKMA diagram are undergirded by more than 30 years of detailed laboratory studies of individual chemical reactions, smog chamber studies of both artificial and real atmospheric mixtures, the careful construction and testing of detailed chemical mechanisms, and numerous applications of atmospheric models that include representations of chemistry, meteorology, and transport. …The basic chemistry is well-understood and accepted by the scientific community as evidenced by its prominent place in the discussions of ozone formation in the 1991 National Academy of Sciences Ozone Report and the more recent NARSTO Ozone Assessment. Therefore, the SR and particularly the ES should be revised to acknowledge these facts.

7a) The SR will be revised to more clearly demonstrate the scientific basis and wide acceptance of the dual nature of NO_X emissions on O_3 concentrations. However, staff will still note the limitations of smog chamber experiments and photochemical models in representing real-world processes. The models are sensitive to a variety of factors and outputs do vary depending on the specifics of any given application. In particular, ambient conditions are now quite low and the earlier smog chamber data do not adequately address photochemistry under low-NO_X conditions. Staff is looking forward to new information that will be available from the next generation of smog chambers. This information will result in improved chemical mechanisms representative of low-NO_X conditions for the photochemical models. Furthermore, the improved time-of-day and day-of-week gridded emission inventories being developed will better represent real world activities than the current inventories do.

8) To fully explain the chemistry of ozone formation, the explanation of NO_X-ozone chemistry on page 2-5 should be expanded to include two additional key NO_X reaction paths and the concept of the photo-stationary-state. The titration reaction of NO with ozone to form NO_2 as well as the class of chain-carrying reactions of NO with radicals to form NO_2 should be included. The two major NO reactions noted above show how NO can both promote and inhibit ozone formation. Finally, the classic concept of the photo-stationary-state should be introduced.

8a) Staff will expand the discussion.

9) The fundamental issue is not whether the NO_X-disbenefit phenomenon occurs, but to what extent it occurs in various locations in California and to what extent other hypotheses may play a role in the ozone weekend effect. As documented in the SR and TSD, the NO_X reduction hypothesis is plausible and is supported by a wide range of analyses that are consistent with it being the primary cause of the weekend effect. In fact, we are not aware of any of the analyses carried out to date that are not consistent with the hypothesis. We recognize, however, that some analyses and observations are consistent with multiple hypotheses. Because of the complexities

of the chemistry and meteorology involved, air quality modeling is needed to distinguish the separate effects of the various shifts in activity and emissions from weekdays to weekends.

9a) Staff is in basic agreement with this comment. Photochemical modeling is the best available tool for addressing the complexities of the Weekend Effect. However, the limitations of modeling must not be ignored, particularly as they might directly influence conclusions (e.g., replication of polluted layers aloft, realistic time-of-day and day-of-week variations in emission inventories).

10) The SR indicates that measurements of VOC/NO_X ratios are an indication of VOC-limited conditions, and notes that the weekday and weekend ratios in the SoCAB are consistent with this hypothesis. But questions are raised concerning the accuracy of the ratios and whether multi-hour average ratios determined by many air parcels affect daily maximum ozone. There are, however, independent analyses with observational indicators by Blanchard that show the extent of reaction at the time of peak ozone is consistent with the hypothesis in those areas with higher weekend ozone.

10a) VOC/NO_X ratios provide insight into the site-specific relationships between ozone precursors and the subsequent peak ozone concentration. Early morning ratios are an important indicator of the afternoon's peak ozone concentration. However, atmospheric processes are complex and staff believes the changing meteorological and environmental conditions between 9 a.m. and the time of peak ozone (some 3-6 hours later) also exert some influence. We know that the atmospheric chemistry during this time drives NO emissions toward NO_2 and HNO_3 and that the oxidizing processes cause VOC/NO_X ratios to increase as NO_X compounds are removed from the photochemical system faster than the VOCs. The unknown factor is how influential the late conditions are compared to the initial conditions. Recent applications of the California Institute of Technology photochemical model (not published yet) indicate that the timing of NO_X emissions do influence the resultant peak O_3 concentrations. The work of Hess, Johnson, et al. referenced in the report indicates that factors subsequent to 6-9 a.m. do have an influence on peak ozone. In fact, Johnson's Smog Production or Extent of Reaction work is the basis for Blanchard's application to data in California. Blanchard's extent of reaction results at the time of peak ozone concentration are very consistent with the spatial pattern of the Weekend Effort and implies that ozone formation in most of the SoCAB is VOC-limited.

11) …the magnitude and even direction of the weekend effect varies significantly across California. The SR indicates that "concentrations of ozone precursors seem to decrease on weekends almost everywhere." (SR on page 1-3) A key issue that needs discussion in the SR is how the various hypotheses can explain these basic facts, including the changes in the weekend effect that have been observed. The atmospheric chemistry of ozone formation (the theory behind the NO_X reduction hypothesis) can explain the presence of a large weekend effect in urban areas. It can explain why the effect is diminished downwind and reverses far downwind. It can also explain the growth in the spatial extent of the weekend effect. It is not clear to us how any of the other hypotheses can explain these differences.

11a) In and of themselves, the other hypotheses cannot explain all of the WEE characteristics. For example, the NO_X Timing hypothesis might explain why O_3 concentrations might be higher on Saturdays than weekdays and higher on Sundays than Saturdays. However, it does not explain why O_3 concentrations historically peaked late in the workweek, transitioned to Saturdays, and more recently transitioned to Sundays. Similarly and perhaps to a greater degree, the Carryover Aloft, and the Soot & Sunlight hypotheses have difficulty explaining the long-term progression of the Weekend Effect. With cleaner fuels, etc., the anticipation is that the particulate matter and soot from mobile sources has declined somewhat and so would the effect of this hypothesis. However, the Weekend Effect has grown in time. Because the NO_X Reduction hypothesis includes O_3 scavenging by NO which occurs whenever and wherever O_3 and NO are present, the NO_X Reduction hypothesis will be a leading factor in WD/WE differences.

12) Another key question that must be answered by this hypothesis [NO_X Reduction] is how ozone can be going down on both weekdays and weekends if NO_X reductions can increase ozone. If the local chemical conditions are in the VOC-limited regime (above and to the left of the ridge line in Figure 2-1), equal reductions of VOC and NO_X will continuously reduce ozone. However, NO_X reductions, by themselves, increase ozone. The draft report of DRI/STI's retrospective analysis of ambient data used an EKMA diagram in this way to show how the chemical state of the SoCAB had changed over the years. They indicated that the VOC and NO_X program had put the basin more into the VOC-limited regime (by reducing VOC somewhat more than NO_X) so that the NO_X-focused shift to weekends now increases ozone more broadly than before. As noted above, accurate long-term VOC data are not available. However, there are other data that corroborate this general view of what has occurred in the basin. Specialized studies that report VOC/NO_X ratios and ambient trend data for individual air toxics (that are present in vehicle exhaust) indicate that VOC concentrations have been dramatically reduced over the past 35 years and VOC/NO_X ratios are lower than in the past. ARB should fully evaluate these sources of data.

12a) Staff agrees with the general premise that VOC/NO_X ratios have declined over the years in the SoCAB. As indicated by the emission estimates in the response to comment #3, ROG (VOC) have been reduced at a greater rate than NO_X emissions. With the greater NO_X than VOC reduction on weekends, the DRI analysis (and NO_X Reduction hypothesis) can explain the Weekend Effect because, in a VOC-limited environment, the NO_X reductions would tend to moderate the ozone decrease anticipated from the ROG reductions by themselves. However, the magnitude of emissions, and not just the ratio of emissions, helps determine the resultant ozone concentrations. As indicated in the table and figure associated with the response to comment #3, ozone decreased the most during the most recent 5-year period when the VOC/NO_X ratio declined the least but NO_X emissions declined the most (both O_3 precursors declined about 20%) since 1975. Most of the specialized studies have limited duration or infrequent sampling schedules that limit the number and significance of the analyses that can be performed.

Comments on NO_X-timing hypothesis

13) While there are differences in the timing as well as the magnitude of emissions between weekdays and weekends, it is unlikely that the timing differences will be able to explain the weekend effect. The ES indicates:

> "The timing difference is potentially important because laboratory experiments indicate that NO_X emitted later in the day can produce ozone more efficiently."

The example discussed in the SR on page 2-7 to illustrate the effect of timing on NO_X efficiency comes from Fig. 4 of Hess et al. 1992. However, the experiment (267L) that was adapted to develop Figure 2-2 had an initial VOC/NO_X ratio of 51. In another experiment with an initial VOC/NO_X ratio of 16.8, the rate of ozone production was decreased when NO was injected.

This is not just a potentially important drawback, it is a major flaw in the interpretation and use of the Hess et al. experiments. The discussion of the NO_X-timing hypothesis should be modified to incorporate this caveat and, therefore, highly qualify the degree of plausibility of the hypothesis

In addition, the results from a series of more pertinent experiments should be added to the discussion. Kelly has carried out numerous captive air irradiations in downtown Detroit, suburban Detroit, Houston and two locations in the SoCAB[1]. These are outdoor smog chamber experiments that use natural sunlight and ambient temperatures and in which ambient air is the primary source of reactants. By operating several chambers simultaneously and by diluting the ambient mixture with clean air or by adding either VOC or NO_X to different chambers, the effects of emission reductions as well as varying the VOC/NO_X ratio can be determined. When Kelly conducted such experiments in rural and remote areas, the photochemistry was NO_X-limited as expected. However, in the urban areas, the photochemistry was VOC-limited and NO additions reduced ozone formation. At several locations, Kelly also filled the chambers at several different times to determine the impact of timing on the ozone formation potential of the mixtures. In suburban Detroit as well as in Houston, the earliest captured mixture produced by far the most ozone. These experiments are important because they were conducted in metropolitan areas that have higher ozone on weekends throughout the area (Detroit) as well as just in portions of the area (Houston). While they do not exactly mimic the NO_X-timing changes in the atmosphere, they do suggest that the photochemical potential of precursors emitted later in the day is reduced rather than increased as posited by the NO_X-timing hypothesis.

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[1] N. A. Kelly, "Characterization of fluorocarbon-film bags as smog chambers," Environ. Sci. Technol., **16**, page 763, 1984; N. A. Kelly, "Ozone/precursor relationships in the Detroit Metropolitan Area derived from captive-air irradiations and an empirical photochemical model," J. Air Pollut. Control Assoc., **35**, page 27, 1985; N. A. Kelly, "An analysis of ozone generation in irradiated Houston air," J. Air Pollut. Control Assoc., **31**, page 565, 1981; N. A. Kelly, "Captive air irradiations in Houston, Texas," Paper No. 80-50.6, presented at the 73rd Air Pollution Control Association Annual Meeting, Montreal, Quebec, Canada, June 1980; N. A. Kelly, "Photochemical ozone formation in outdoor smog chambers and its sensitivity to changes in precursors at a suburban Detroit site," in Wolff G. T., Hanish J. L. and Schere K. L.(editors), "The Scientific and Technical Issues Facing Post-1987 Ozone Control Strategies, Air Pollution Control Association, Pittsburgh, PA, pages 110-123, 1988; N. A. Kelly and R. F. Gunst, "Response of ozone to changes in hydrocarbon and nitrogen oxide concentrations in outdoor smog chambers filled with Los Angeles air," Atmos. Environ., **24**, Part A, page 2991, 1990.

Because of the complexities of ozone formation, photochemical modeling is required to fully evaluate the NO_X timing hypothesis. The ENVIRON proximate modeling can be used to evaluate traffic-induced NO_X changes. The activity data in the TSD suggests that there are two parts to the NO_X-timing changes. First, heavy-duty truck activity and NO_X emissions are expected to be substantially reduced during all hours on weekend days. Second, car and light truck activity is shifted in time because of the greatly reduced morning commute on weekend days. Since these two categories have different activity patterns and have different regulatory requirements, the modeling should evaluate the activity shifts both separately and in combination.

13a) Staff believes the Hess work on the impact on O_3 of additional NO_X emissions is pertinent. It is true that the VOC/NO_X ratio in the example was 51 and not representative of typical ambient conditions. The point of the illustration is that as ozone formation becomes more NO_X-limited in the afternoon, fresh emissions of NO_X can enhance O_3 formation. The author of the comment implied that at more typical VOC/NO_X ratios (16.8) that the O_3 formation was <u>decreased</u> with the addition of NO_X; this is not true. The rate of O_3 formation slowed slightly but the amount of O_3 continued to increase. Thus, is not unlike what we observe in the atmosphere on weekends. The O_3 formation begins earlier and might be expected to become NO_X-limited sooner. However, the addition of more NO_X (and VOC) when O3 formation is becoming precursor limited allows O_3 to continue forming at essentially the same rate. Thus, the ozone formation rate does not change during the morning but, in effect, continues longer than would have been the case had not additional O_3 precursors been added. In the captive air irradiation experiments referenced in the comment, the initial precursors were added later in the morning so it's no surprise they produced less ozone.

The proximate modeling results from Environ's work will be helpful but may be limited unless the inputs are realistic and base conditions are replicated well. Environ is currently waiting for resolution of some questions about emission outputs from the EMFAC2000 model.

The suggestion about also separating the HDD and LDVs in the modeling analyses is a good idea (to address independent as well as synergistic effects).

Comments on carryover aloft hypothesis

14) This hypothesis assumes that carryover aloft occurs on all days of the week, but that carryover exerts a greater influence on weekends. …Additional data on the composition of layers aloft would be helpful, but existing models can be applied now to determine the sensitivity of ground-level ozone to the relevant parameters.

We have three additional comments on this hypothesis - two that relate to its plausibility and one that relates to the implications of the hypothesis for regulatory NO_X reductions. First, the premise for this hypothesis, that ozone carryover is the same from day-to-day but ground-level NO_X emissions are different on weekdays and weekends is not correct. In reality in the SoCAB, peak ozone levels during mid-

day when the atmosphere is well-mixed are now highest on Sunday. This means that the ozone available for carryover is not the same from day to day. Since ozone, on average, is lower on Mondays than on Sundays, the carryover of ozone from Sunday to Monday, on average, is substantially greater than the carryover of ozone from Monday to Tuesday. Since the morning NO_X emissions on Monday and Tuesday are comparable, the impact of different levels of carryover can be compared by evaluating the levels of ground-level ozone on Monday and Tuesday afternoon. These levels are similar, which argues that carryover is not a dominant factor in determining mid-afternoon ozone levels.

Second, if the carryover hypothesis is correct, it should be able to explain the spatial extent of the weekend effect. The hypothesis would predict that ozone should be higher on weekends at all sites with significant weekday NO_X emissions and the same on weekdays and weekends at sites with little or no NO_X emissions. The data, however, indicate that there are urban sites in the southeast U. S. (with high biogenic emissions) and rural sites where ozone is lower on weekends. This suggests that VOC/NO_X chemistry rather than carryover is the primary cause of the weekend effect.

Finally, if the carryover aloft hypothesis is true, the NO_X reduction program over the past several decades has made NO_X become more efficient at making ozone on weekdays as well as on weekends. And importantly, future NO_X reductions will make NO_X more efficient at making ozone on both weekdays and weekends. Thus, if this hypothesis is true, the impact of carryover has been to reduce the benefits from NO_X emission controls. As such, the implication of this hypothesis for regulatory NO_X reductions is the same as for the NO_X reduction hypothesis. In either case, less NO_X means more ozone. So if further study supports this hypothesis as a significant cause or the primary cause of higher weekend ozone, the policy implications are that NO_X reductions should be either avoided or approached cautiously.

14a) Staff revised the write-up on this hypothesis to make it easier to understand as the comments appear to be based on misunderstandings. The staff did not state that ozone carryover is necessarily the same from day-to-day. The ozone aloft will vary depending on the variation by day-of-the-week and, probably more importantly, by meteorological conditions. Nevertheless, the point that carryover is not the dominant factor in determining afternoon ozone levels is acknowledged. The second comment addresses the spatial variations and suggests that chemistry is more of a factor than carryover. However, the background air quality and meteorology can have significant influence. With the coastal marine layer in the western SoCAB, the influence of ozone carryover aloft will generally have little or no effect in coastal areas, more effect in the peak ozone regions of the basin, and less influence at the more rural downwind sites. The last paragraph of this section (the third (last) comment) misinterprets the hypothesis and the implications for NO_X control. Hopefully, the rewrite reduces the chance of misinterpretation.

Many years ago, ozone concentrations tended to be the minimum of the week on Monday and the maximum on Thursday, thus implying some influence of carryover because emissions are presumably down on weekends and fairly constant on

workdays. Now, ozone concentrations on Monday and Thursday are similar to other weekdays. As emission controls reduce precursors and ozone, the amount of carryover would be expected to also decline although the relative impact might not. Ozone formation in much of the SoCAB may have moved to a VOC-limited environment that could accentuate the impact of carryover (relatively rich in VOC). This possibility is supported by several observations: 1) VOC emissions have always been reduced more than NO_X emissions, 2) peak day ozone has shifted from Thursday to Saturday to Sunday despite progressively lower NO_X emissions on these days of the week, and 3) Monday is no longer the minimum ozone day of the week as might be anticipated with the effects of reduced ozone precursor carryover and the relative increase in ozone scavenging by fresh NO emissions on Monday morning.

Comments on soot and sunlight hypothesis

15) While the soot and sunlight hypothesis is plausible as a factor that would increase ozone on weekends, analyses carried out for ARB in an earlier study indicate that solar radiation is not significantly higher on weekends. In addition, the earlier analyses found that there is a small temperature decrease on weekends that, by itself, could reduce ozone formation on weekends by from 5 to 10 ppb. These earlier analyses are discussed in more detail below. On balance, the measured changes in meteorological variables are too small to account for the weekend effect and, if anything, may cause lower ozone formation on weekends.

In addition, because soot levels have been decreasing in California, the difference between weekday and weekend soot levels is also becoming smaller. Thus, the magnitude of any soot and sunlight effect has been getting smaller over time. This is inconsistent with the increase in the strength and spatial extent of the ozone weekend effect. Finally, since soot levels are forecast to continue decreasing, the effect will continue to get smaller in the future. For these reasons, the soot and sunlight effect should be put in the category of plausible but not likely to be a significant factor.

While expanded measurements and analyses can never do any harm, it is extremely unlikely that the soot and sunlight hypothesis will be able to explain any significant fraction of the weekend effect. In addition, any research program should evaluate temperature effects that would tend to offset the soot effects.

15a) Staff agrees that the initial studies in this area do not indicate an appreciable influence. However, the databases to support such studies are not extensive nor necessarily of high quality. With cleaner fuels and other controls, it is reasonable to think that particulate matter emissions from motor vehicles may have declined slightly over the years and thus lessening, not increasing, the Weekend Effect if this hypothesis were a major factor. Furthermore, future particulate matter controls on motor vehicles would make this contribution to the Weekend Effect even smaller. On the other hand, some people speculate that while control efforts may have reduced the total mass of particulate emissions, they have increased the number of particles. Some preliminary, unpublished photochemical modeling with the California Institute of Technology model indicates that changes in actinic flux on the

order of 10-20 percent could help explain a significant portion of the Weekend Effect. It seems prudent to staff to embark on some more definitive data collection and analysis efforts as resources permit.

Comments on control of NO_X for other purposes

16) Conclusion # 3 of the SR… …discussion of conclusion # 4… are not supported by the material in the TSD or in the Findings section of the SR. One of the bullet points in Finding # 14 [PM10-nitrates] … the conclusions and summary sections of the SR fail to inform the reader that (1) nitrate is not substantially lower on weekends, and that (2) the likely reason is that the higher photochemical activity on weekends (as evidenced by ozone formation) is increasing the rate of nitrate formation. The important policy implication that should be provided to the reader is that reducing NO_X may not necessarily reduce nitrate concentrations if it also increases ozone formation.

16a) Staff has included additional discussion on secondary pollutant formation processes in the report. Staff is not convinced that the current nitrate data do not indicate a weekday/weekend variation. As noted in Finding #14, 1997-1999 nitrate data collected in the SoCAB indicate that PM10-nitrate was lower on the weekends than on weekdays by an average of 13 percent and occurred at 14 of the 15 locations. The current measurements are based on a one-in-six-day sampling schedule of filter-based measurements. There are inherent deficiencies in this measurement technique and sampling frequency. More robust data collection and analysis are necessary to better address this uncertainty.

Summary

17) …additional information and analysis can reduce the number of plausible hypotheses so that they can be evaluated with photochemical modeling in the near future. Based [on] the discussion in the body of these comments, several of the statements and conclusions in the Staff Report need to be revised.

For each hypothesis, several expectations are listed. It would be more appropriate to start with the findings (from ARB and other current analyses) and evaluate the hypotheses against all the findings. In this way, we believe the number of plausible hypotheses will be reduced.

17a) The following observations are from the findings/observations noted in the ARB Staff Report and Technical Support Document. The consistency of each observation with the various hypotheses of the Weekend Effect is noted.

Observation	H #1	H #2	H #3	H #4	H #5	H #6
Ground-level VOC/NO_X ratios are in the VOC-limited regime for O_3 formation	Y					
Ground-level VOC/NO_X ratios increase during daylight hours		Y				
Ground-level VOC/NO_X ratios are higher on WEs than on WDs	Y	Y	Y	Y	Y	
Ground-level NO_2/NO ratios are higher on WEs than on WDs	Y	Y				
NO_X concentrations on WEs increase later but faster than on WDs		Y				
Traffic and precursor concentrations are greater on Fr & Sa nites			Y			
Precursor concentrations at sunrise are similar on WEs and WDs			N			
[O_3]s aloft (typically only measured during episodes) tend to be higher than background levels				Y		
VOC/NO_X ratios are higher aloft that at ground-level				Y		
Precursor concentrations are lower on WEs than WDs at almost all sites					N	
WIM data indicate lower traffic on WEs than WDs at all but peripheral locations					N	
HD truck traffic is down dramatically on WEs compared to WDs						Y
UV radiation decreases only slightly from WDs to WEs						N
The WE Effect is primarily evident in major urban areas	Y	Y	Y			
The WE Effect has expanded eastward over the SoCAB over the years	Y	Y	Y			
Ozone trends down on both WDs & WEs but slower on WEs	Y	N				
Ozone trends down fastest during period of greatest NO_X emission reductions	N	Y				

H #1 – NO_X Reduction hypothesis
H #2 – NO_X Timing hypothesis
H #3 – Carryover at ground-level hypothesis
H #4 – Carryover Aloft hypothesis
H #5 – Increased Emissions hypothesis
H #6 – Soot and Sunlight hypothesis

Major Comments from Envair (see Appendix B for full text)

Executive Summary

1) A key commonality of the three plausible hypotheses with supporting data is that all involve the effects of NO_X on ozone; the hypotheses are in fact tightly linked. They differ in the degree of emphasis placed on the effects of mid-day emissions of NO_X, and the relative contributions of carryover ozone to peak ozone concentrations.

1a) NO_X figures prominently in the hypotheses because of its dual nature in promoting and inhibiting ozone formation. The hypotheses must account for the morning pulse of emissions available for photochemical production being smaller and later on weekends than on weekdays. To have increased ozone on weekends then the relatively greater reduction in NO_X emissions compared to VOC must increase ozone formation or factors changing the chemical environment must be different. Although most hypotheses include a NO_X component, the implications for NO_X control can be different.

2) Ongoing field studies are already in place to provide further data for understanding the weekend effect (Fujita et al., 2000). The need for an additional comprehensive and extended field program to further distinguish among the plausible explanations of the weekend effect is not apparent. A more productive use of resources would be to focus on evaluating geographically-targeted ozone control strategies, rather than on testing hypotheses of the weekend effect. Further analysis of data from the 1997 Southern California Ozone Study (SCOS97) and the ongoing Central California Ozone Study (CCOS) projects, along with modeling studies, should be pursued. An additional topic meriting further investigation is the effect of VOC and NO_X reductions on aerosol nitrate formation. Existing studies indicate that aerosol ammonium-nitrate formation in California is typically not limited by the availability of ammonia. However, existing work from the San Joaquin Valley Integrated Monitoring Study of 1995 (IMS95) also suggests that VOC reductions may reduce the rate of aerosol nitrate formation more effectively than NO_X reductions in areas where ozone formation is VOC limited. This topic should be investigated through analyses of data from the Central California Regional Particulate Air Quality Study (CRPAQS), along with modeling studies.

2a) Additional data (field studies) are needed to definitively and thoroughly address unknowns and uncertainties associated with the Weekend Effect. Probably the most critical need is for activity data for the generation of day-specific emission inventories. Ultimately, gridded day-of-week emission inventories with hourly resolution will be needed for definitive testing of hypotheses of the Weekend Effect. Other data needs include better information on VOC and NO_X speciation, atmospheric processes aloft, and accurate modeling of these parameters. The difficulty with special studies is that the large meteorological variations often obscure other processes and limit the statistical significance.

In regard to using information from previous aerosol studies in the San Joaquin Valley for modeling studies, it is the staff's belief that secondary aerosol formation processes are significantly different in the San Joaquin Valley and South Coast. In

addition, the analyses supporting VOC controls to reduce nitrates (i.e., NO_3) are limited and need additional confirmation. Furthermore, aerosol models, although dramatically improved, are still in need of refinement and results must be interpreted in terms of the assumptions and model limitations.

Why Does the Weekend Effect Occur?

3) Recommendations in the CARB report include steps for acquiring data that would permit further evaluation of the "soot and sunlight" hypothesis. However, the need for such an evaluation should not be overrated. As discussed below, existing data already support three other hypotheses considered plausible by the CARB report - thus, measurements now indicate that the "soot and sunlight" hypothesis cannot be the only cause of the weekend effect.

3a) The limited data and analysis to date suggest that the Soot & Sunlight hypothesis does not explain a large portion of the Weekend Effect. However, the limited amount of data, its uncertain quality, and the dramatic shift in heavy-duty diesel activity on weekends encourages some refinements in order to be definitive about its relative contribution. Some preliminary photochemical modeling by Dr. Donald Dabdub (UC-Irvine) indicates that increased ultraviolet radiation can have a significant influence on weekend ozone concentrations. However, the limited amount of current UV data indicate a very small increase on weekends - not enough to have a significant effect on ozone concentrations. On the other hand, theoretical work by Liao (1999) indicates a potentially stronger effect from soot particles, particularly when cloud layers are involved.

4) The CARB report also notes that aerosol nitrate, derived from NO_X, can constitute a substantial portion of fine particulate mass. However, during warmer months when ozone concentrations reach high values, aerosol nitrate concentrations are low at most locations; conversely, aerosol nitrate concentrations are highest during winter months, when ozone concentrations are lowest. The temperature dependence of aerosol nitrate is related to an equilibrium reaction between aerosol nitrate and its gas-phase precursors, nitric acid and ammonia, which favors the gas-phase species as temperatures increase. Thus, aerosol nitrate is generally not a significant component of the aerosol mass during the time periods of interest for understanding the ozone weekend effect. However, aerosol nitrate formation is affected by both VOC and NO_X emission levels, as discussed later. Therefore, both ozone and aerosol formation need to be addressed in considering emission control strategies.

4a) Mr. Blanchard's comments appear to be based primarily on data from the Central Valley of California. The formation of nitrate aerosols is dependent on several factors in addition to temperature (e.g., ammonia, humidity). Although both the Central Valley and the South Coast have ammonia sources and cool, moist meteorological conditions, the most conducive meteorology occurs at different times of the year. While winter is the dominant season in the Central Valley, the regular on-shore flow of the coastal marine layer can provide cool and moist conditions throughout the year. While high ozone and nitrate concentrations do not generally occur on the same day, they can occur during the same season. The bottom line

though, which Mr. Blanchard and staff agree on, is that both ozone and aerosol formation need to be addressed when considering emission control strategies.

Fresh NOX emissions, which primarily consist of nitric oxide (NO) undergo reactions with ozone and peroxy radicals to form nitrogen dioxide (NO_2). The NO_2 can be directly converted to nitric acid via the homogenous gas-phase reaction with the hydroxyl radical. This is the principal formation mechanism for nitric acid in the daytime. The principal chemical loss process for gas-phase nitric acid is its reaction with gaseous ammonia to form ammonium nitrate (NH_4NO_3). This reaction, which is reversible, is believed to be the primary source of fine (<2.5 µm diameter) nitrate aerosol in California's urban air.

The atmospheric chemistry leading to formation of particulate nitrate is fairly complicated. The rates of transformations depend on the concentrations of many intermediate species (including ammonia and radical species) involved in the photochemical system of reactive organic gases and NO_X. Ambient concentrations of secondary particles are not necessarily proportional to the quantities of their precursor emissions since the rates at which they form and their gas/particle equilibria may be controlled by factors other than the concentration of the precursor gas. The rate of NO_X oxidation and the branching ratio between inorganic and organic nitrates depend on the specific environmental conditions (e.g., temperature and relative humidity) in addition to reactant concentrations.

PM-nitrate concentrations vary seasonally according to the nature of the predominant emission and meteorological factors in the area. However, PM-nitrate concentrations exhibit less seasonal variation in the South Coast Air Basin than in other air basins (e.g., the Sacramento valley Air Basin and San Joaquin Valley Air Basin where concentrations are higher during winter than during summer). The limited seasonal variation in PM-nitrate concentrations in the SoCAB is rather unique compared to other areas of California. Apparently, secondary particulate formation during the summer months in the SoCAB is commensurate with the typical high production during the cooler months of the winter. Although nitrate production is greatest during the winter months, the nitrate fraction remains significant during the summer in the SoCAB.

5) In these statements of the three hypotheses, a key commonality is that all three involve the effects of NO_X on ozone: in each case, fresh NO emissions lower ozone concentrations by virtue of the reaction of NO with ozone, and they reduce rates of ozone formation by lowering radical concentrations. These hypotheses are therefore tightly linked, and are not mutually exclusive. They differ in the degree of emphasis placed on the effects of mid-day emissions of NO_X, and the relative contributions of carryover ozone to peak ozone concentrations. The hypotheses were formulated as distinct explanations, because the CARB report argues that the NO_X-reduction and NO_X timing hypotheses "have substantially different policy implications with respect to NO_X controls as an ozone control measure." Similarly, in situations where there may be substantial contributions of carryover ozone to peak values, control strategies may differ from those used where little carryover occurs.

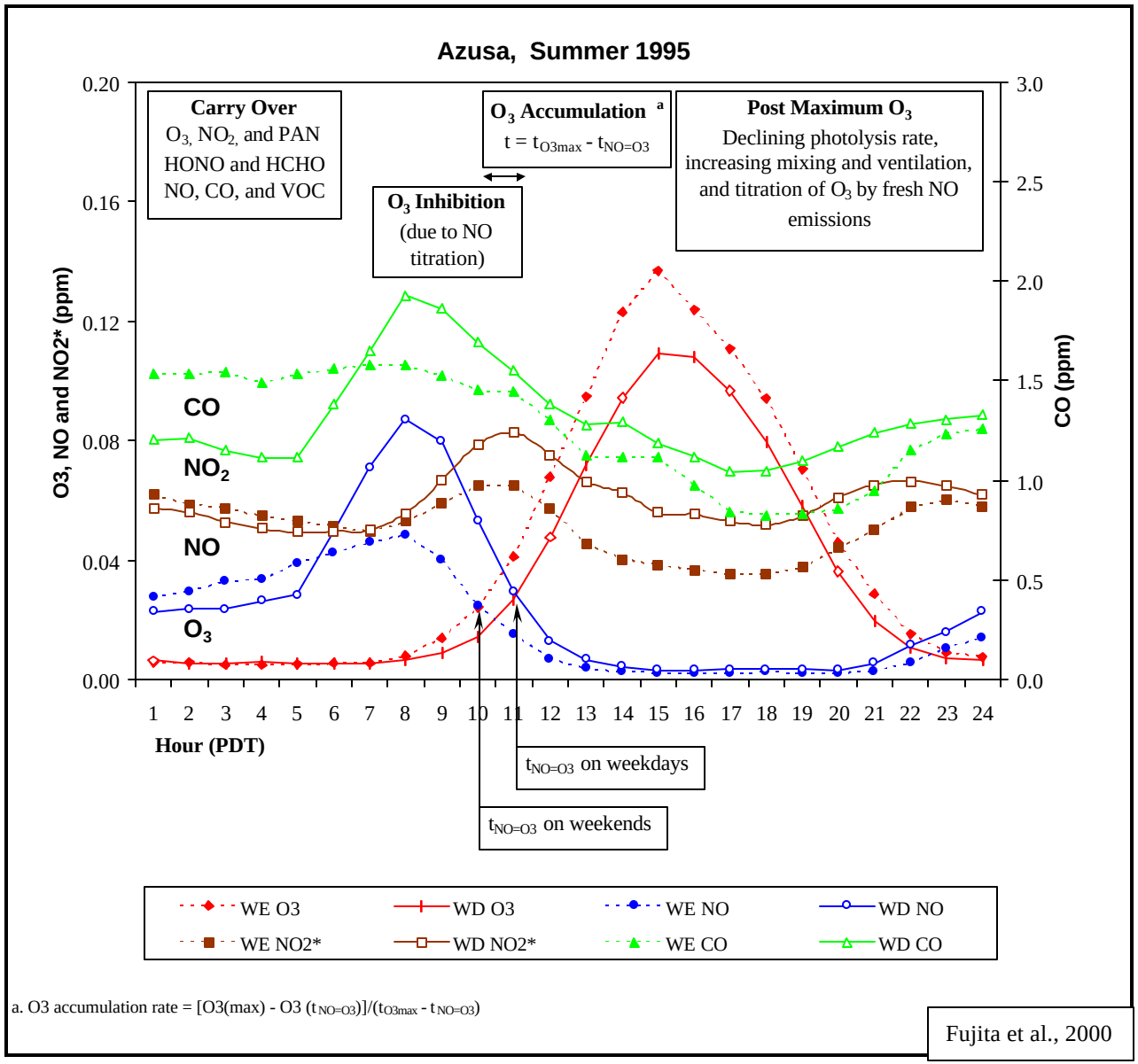
5a) no comment

6) The same evidence supports the initial premise of the NO_X-timing hypothesis, but evidence for its second premise is lacking:

> "Because less NO_X is present to depress the concentration of radicals, the photochemical system becomes more active earlier in the day. As activities and emissions increase toward mid-day, the fresh NO_X enters this more active system, participates in ozone-generating reactions more efficiently, and leads to higher weekend ozone compared to weekdays."

As found by all studies and noted above, the photochemical system does become active earlier on weekends. However, the rates of accumulation of ozone do not accelerate during the middle of the day at sites showing a weekend effect. Although Fujita et al. (2000) showed that 9 the 13 sites in the South Coast Air Basin showed a higher rate of ozone accumulation on Sundays during the period 1995 through 1998, no sites showed an acceleration of ozone formation just prior to the time of occurrence of the peak ozone concentration. Moreover, diurnal profiles show that the differences between weekend and weekday ozone concentrations begin early, with the earlier weekend "starting" time for ozone formation (when O_3 and NO concentrations become equal), and continue throughout the morning; the weekend effect does not occur as a sudden acceleration of ozone production at mid-day (see Figures 3 through 5 for examples). However, in some locations the data are not inconsistent with a small mid-day effect coinciding with the apparent input of fresh emissions, but this effect is modest in comparison with the differences between weekday and weekend ozone concentrations that can be traced through to earlier in the morning.

6a) During mid-day, motor vehicle activity (and presumably emissions) is comparable on weekdays and weekends. If ozone formation on the weekend is not VOC-limited by mid-morning because the photochemistry became efficient sooner and the NO_X concentrations were relatively lower than the VOC concentrations initially compared to weekdays, the mid-day emissions of both VOC and NO_X can act as fuel for the formation of additional ozone. The precursors will continue producing more ozone until its formation becomes precursor- or light-limited. The ozone formation rate (efficiency) doesn't necessarily change dramatically but, without VOC as a limiting precursor initially, ozone production occurs a couple of hours longer on weekends than on weekdays and thus resulting in higher ozone concentrations. Looking at the weekday and weekend diurnal profiles of ozone (e.g., Chapter 2 of the TSD), one sees a tendency for the weekend ozone peak to occur slightly earlier in the western portion of the SoCAB and slightly later in the eastern portion of the SoCAB. Looking at the data figure below (courtesy of Fujita, 2000) from Azusa (central portion of the basin where the time of the weekday and weekend peaks in concentration is similar), it is apparent that the hourly differences in ozone concentrations (WE - WD) increase until the peak hour. Furthermore, the hour-by-hour formation rate on weekends is slightly faster than on weekdays at Azusa. Interestingly, the hourly difference between weekend and weekday concentrations is essentially the same magnitude but opposite sign as the hourly difference between weekend and weekday NO_2 concentrations. In effect, the total oxidant (O_3 + NO_2) levels are similar on weekdays and weekends but the equilibrium between the oxidants shifted.



a. O3 accumulation rate = [O3(max) - O3 ($t_{NO=O3}$)]/(t_{O3max} - $t_{NO=O3}$)

Fujita et al., 2000

7) Diurnal concentration profiles also show that ambient CO and NO_X concentrations after about 4 a.m. on weekends are reasonably parallel with weekday concentrations. Some differences do occur, perhaps suggesting more sustained weekend emissions levels between about 8 and 10 a.m., or somewhat greater increases (but not greater concentrations) of precursor concentrations between approximately 10 a.m. and 1 p.m. than on weekdays. On the whole, however, the weekend precursor concentration profiles resemble weekday profiles; they do not resemble the hypothetical weekend emission profile shown as Figure 2-4 of the CARB report.

7a) Figure 2-4 is a conceptual profile of diurnal variations in emissions, not ambient concentrations. Ambient concentration profiles are not exactly similar to the emission profiles because concentrations are a function of emissions, meteorology, and chemistry. In particular, the meteorology enhances the effects of emissions around sunrise and sunset when the air is stable and minimizes the effects of emissions during the middle of the day when atmospheric dispersion is usually greatest. The Fujita et al. figure (shown above) of concentrations at Azusa does not show relatively parallel concentrations of CO and NO_X for the WD/WE profiles. However, the NO_2 and O_3 profiles are the same general shape on WDs and WEs and the sum of NO_2 and O_3 is quite constant between WDs and WEs.

8) As noted in the CARB report (Figure 2-2), chamber experiments support the idea that ozone production can be accelerated in a system that has reached a state of NO_X limitation by injecting fresh NO_X. However, the weekend effect occurs at VOC-limited sites, not NO_X-limited locations. Therefore, the relevance of the cited chamber experiments as an explanation of the weekend effect is not apparent.

8a) This is probably the root of many of the comments on the report and why staff is unwilling to "jump on the NO_X reduction bandwagon" at this point. The limited number of monitoring sites with VOC and NO_X data indicate that ozone formation is probably VOC-limited during the morning hours. The even more limited data on afternoon conditions indicates that VOC/NO_X ratios increase from the initial morning conditions but ozone formation probably still is not NO_X-limited. Staff has a few concerns about analysts deducing/assuming that ozone formation is therefore VOC-limited throughout the day at all locations. First, after several hours of photochemistry, many of the hydrocarbons in the atmosphere have become partially oxidized and are not detected by routine monitoring methods. A recent study (Paulson, 1999) indicated that standard VOC measurements can be on the order of 30% low. Even standard gas chromatography methods probably underestimate the true amount of VOCs in atmospheric samples (Lewis et al., 2000). Furthermore, current NO_X monitoring techniques tend to overestimate the NO_X concentrations (particularly during the day) because they include additional oxidized forms of NO_X (e.g., HNO_3, PAN). These monitoring biases indicate that NMOC/NO_X ratios are higher than ambient data indicate. In addition, NO_X concentrations, because of their high reactivity, have declined to typical detection limits. Most monitoring stations are in urban locations near heavily traveled roadways and thus might not be fully representative of a spatially-weighted VOC/NO_X ratio due to the impact of fresh emissions. Furthermore, chemistry modules in photochemical models do not always

represent low-NO_X chemical reactions well. In essence then, there is sufficient uncertainty about VOC/NO_X ratios during the period of peak photochemistry that staff is reluctant to say that ozone formation is VOC-limited throughout the day. The essence of the NO_X Timing hypothesis is that ozone formation is no longer VOC-limited (and may even be NO_X-limited) by mid-day when weekend emissions are comparable to weekday emissions. If ozone formation has not already become light-limited, these emissions will contribute to increased ozone formation; weekends more so than weekdays because the VOC/NO_X ratios are higher.

9) Those aspects of the "NO_X-timing" hypothesis that have not been resolved by existing data appear to be amenable to reasonably straight-forward analyses using either photochemical box models or three-dimensional gridded models. The need for "Accurate, artifact free measurements of VOCs and NO_X in three dimensions" (Austin et al., 2000) may not be sufficiently pressing to warrant the expense of special field sampling.

9a) Staff concurs that special field sampling to collect the requisite types and amounts of data (especially aloft) would be very expensive. Staff however is not confident that currently available modeling applications would necessarily arrive at the correct conclusion for the correct reasons. Staff believes that additional improvements are needed in models before definitive progress can be made on this front (e.g., meteorological module on handling layers aloft, emission inventories reflective of the spatial, temporal, and chemical variations in emissions, chemistry modules appropriate for low NO_X conditions).

10) Ample evidence supports the existence of higher concentrations of ozone aloft. As noted in the CARB report, during morning hours of the SCOS97 when ozone concentrations at surface sites were depleted, concentrations were often in the range of 40 to 80 ppbv at ~400 m to 4000 m agl; occasionally, concentrations of 140 ppbv or more were observed. During the 1987 Southern California Air Quality Study (SCAQS), aloft ozone concentrations exceeding 200 pbbv were recorded (Roberts and Main, 1992). Aircraft measurements recorded average aloft ozone concentrations in the range of 60 to 120 ppbv in the San Joaquin Valley and Bay Area during the 1990 San Joaquin Valley Air Quality Study (SJVAQS) (Blumenthal et al., 1997).

10a) Staff agrees and has no comment.

11) As noted in the CARB report (Austin et al., 2000), it is likely that air masses aloft are typically more aged than those at the surface, implying that further formation of ozone aloft may often be limited by the availability of NO_X. Analyses of surface and aloft measurements of NO_X and hydrocarbons collected at various locations in the San Francisco Bay Area and the San Joaquin Valley during the 1990 SJVAQS have provided evidence that aloft air masses are more aged than surface samples during early morning hours, and are more aged than afternoon aloft samples (Blumenthal et al., 1997). These conclusions were supported by comparing ratios of VOC/NO_X, xylenes/benzene, and toluene/benzene (xylenes and toluene react more rapidly than benzene, so departures of those ratios from the ratios characteristic of fresh emissions provides an indication of aging). Data from other locations (see Figure 6)

show that situations occur where early morning surface layers have low concentrations of ozone, depleted by reaction with fresh NO_X emissions, whereas NO_X levels in layers aloft are low and ozone concentrations have reached the maximum levels possible without further input of fresh emissions. In the examples shown, ozone formation remained VOC-limited throughout the following daytime hours at the urban locations.

11a) Staff is not convinced that ozone concentrations observed aloft in the morning have "reached the maximum levels possible without further input of fresh emissions." Ozone lidar data collected during SCOS97-NARSTO indicated the potential for ozone concentrations aloft to increase after sunrise but before the lower atmosphere became sufficiently unstable to carry fresh emissions aloft to the layer of increasing ozone. Additional work is needed to investigate whether the increase in ozone concentrations aloft (between 500 and 1500 feet) was due to photochemistry or to transport over the lidar site. For various reasons noted earlier, staff is not totally convinced that ozone formation remains VOC-limited throughout daylight hours at urban locations.

12) Many locations showing aged air aloft nonetheless exhibit same-day surface concentrations of ozone and precursor species that are indicative of VOC limitation. Specific cases must be studied carefully using modeling and a variety of data analyses to establish the probable consequences of various levels and combinations of VOC or NO_X emission reductions.

12a) The presence of ozone aloft does not necessarily mean that surface concentrations (and processes) will be affected by it. Staff agrees that studies need to be carefully planned to address specific uncertainties and the consequences under a variety of conditions.

13) The CARB report concludes that each of the three hypotheses discussed here is plausible, but none is proven and all may play some role. However, the CARB report and all other studies found considerable evidence to support the NO_X-reduction hypothesis, and that hypothesis is consistent with expectations derived from theory and from modeling studies. Also, sufficient evidence exists to show that aloft ozone concentrations exceed surface concentrations at many times and places, and do contribute to ground-level ozone values as vertical mixing occurs during the day. In the next section, control implications are considered. Indeed, what is needed is not further testing of these hypotheses. Rather, the primary need is to delineate control strategies that are effective at all times and places, including areas that are VOC-limited, areas that are NO_X limited, and areas dominated by transported ozone.

13a) In essence, this has been the policy of the Board – adopting stringent ROG and NOX controls on ubiquitous mobile sources to reduce precursors of both ozone and PM. ROG controls will have more benefit in urban source regions and NOX control will have most benefit in downwind receptor regions.

What are the Implications for Ozone Control Strategies?

14) Because of the range of conditions occurring throughout California, statewide emission-reduction strategies must include both VOC and NO_X. Locally, however, ozone formation is either limited by VOC or by NO_X, and the most effective local control strategies will target the limiting precursor in each area. As reported in Austin et al. (2000), ozone concentrations have trended strongly downward in the South Coast Air Basin since 1980, so the control strategies that have been employed have indeed been successful. However, the data cannot show that those strategies have been optimal, as no alternatives to the historical emission control program exist for comparison. …Unlike the difference between weekdays and weekends, the NO_X reductions occurring over the period 1980 through 1998 were accompanied by even stronger VOC reductions; thus, ozone concentrations declined throughout the South Coast Basin and the Bay Area, even at sites that exhibit a weekend effect.

14a) It is true that we do not know definitively what strategy was or will be most effective. We can only note that the most rapid improvement in ozone air quality observed since control programs were implemented occurred in the last 5 - 10 years when VOC, and particularly NO_X, reductions were large. The rate of NO_X reductions has always been the same or less than the rate of VOC reductions and staff recommends continued adherence to this approach because of the NO_X Reduction hypothesis. Staff agrees that local control strategies must be developed that efficiently address the unique characteristics of ozone formation in each area.

15) These observations are testable using three-dimensional model studies with appropriate databases and model evaluation.

15a) Staff reiterates the limitations of models without proper spatial and temporal characterization of emissions and proper replication of atmospheric processes aloft and photochemical processes.

16) However, like ozone, the rate of formation of nitric acid may be limited either by radicals or by NO_X. Therefore, in some situations, aerosol nitrate formation may be more effectively reduced through reductions of VOC than NO_X emissions (Pun and Seigneur, 1999). More specifically, existing work suggests that VOC reductions may reduce the rate of aerosol nitrate formation especially in areas where ozone formation is VOC limited. Additional research efforts should be directed to this topic.

16a) In some cases, VOC controls may be necessary to reduce particulate nitrate. Staff encourages further research in this area.

What Research Efforts are Needed?

17) The CARB report concludes that "Accurate, artifact free measurements of VOCs and NO_X in three dimensions are needed to assess the contributions of the "NO_X-reduction" hypothesis, the "NO_X-timing" hypothesis, and the "Carryover aloft" hypothesis." Yet, regardless of the relative contributions of each process to the overall weekend effect, ample scientific evidence exists to indicate that the range of conditions in California requires geographically-focused reductions of VOC and NO_X emissions, with emphasis on VOC reductions in areas known to be strongly VOC-

limited (e.g., most of the San Francisco Bay Area, South Coast Air Basin, and San Diego Air Basin) and NO_X reductions where ozone is NO_X-limited. Since the latter require statewide strategies in some cases (e.g., motor vehicles), careful consideration should be given to the balance of VOC and NO_X controls imposed within the coastal metropolitan areas. Regardless of the exact contributions of each plausible cause to the overall weekend effect, the undisputed magnitudes of the increased weekend ozone concentrations within the San Francisco Bay Area, South Coast Air Basin, San Diego Air Basin, and some urban locations within the Central Valley indicate that control strategies in which NO_X emission reductions exceed VOC emission reductions are likely to aggravate ozone concentrations in those areas. The weekend effect provides a clear test case.

17a) As noted before, staff is not convinced that the Weekend Effect provides a clear test case of the impacts associated with future NO_X controls. However, staff does not disagree with Mr. Blanchard's points.

18) Ongoing field studies are already in place to provide further data for understanding the weekend effect (Fujita et al., 2000). Thus, a more productive use of resources would be to focus on evaluating geographically-targeted ozone control strategies, rather than on testing hypotheses of the weekend effect. Further analysis of data from the SCOS97 and CCOS projects, along with modeling studies, should be pursued. An additional topic meriting further investigation is the effect of VOC and NO_X reductions on aerosol nitrate formation. This research need was previously identified by analyses conducted under the Central California Regional Particulate Air Quality Study (CRPAQS) and should be investigated further using data from the Central California Regional Particulate Air Quality Study, along with modeling studies.

19a) Please see the above responses to 2a) and 17a).

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